

# (12) UK Patent Application (19) GB (11) 2 272 444 (13) A

(43) Date of A Publication 18.05.1994

(21) Application No 9223792.4

(22) Date of Filing 13.11.1992

(71) Applicant(s)  
**Minnesota Mining and Manufacturing Company**  
  
**(Incorporated in USA - Delaware)**  
  
**PO Box 33427, 3M Center, Saint Paul,**  
**Minnesota 55144-1000, United States of America**

(72) Inventor(s)  
**Keith Paul Parsons**  
**Alan J Lindsay**

(74) Agent and/or Address for Service  
**Lloyd Wise, Tregear & Co**  
**Norman House, 105-109 Strand, LONDON, WC2R 0AE,**  
**United Kingdom**

(51) INT CL<sup>5</sup>  
**C08F 8/40 , C07F 9/44 , C08K 5/5399 , C08L 101/00**

(52) UK CL (Edition M )  
**C3J JCE**  
**C3K KEC K102 K123 K201 K210 K253**  
**C3M MA MXC M114 M123C M124C M125C M139**  
**M140 M142 M144 M150C M153C M170**  
**C3R RSM R7N5A R7N5B R7N6 R7PX**  
**C3W W100 W201 W207 W211 W217 W218 W227**  
**W312 W330**  
**U1S S1362 S1420 S2056 S3011**

(56) Documents Cited  
**GB 1475685 A GB 1428457 A GB 0657081 A**  
**EP 0003067 A1**

(58) Field of Search  
**UK CL (Edition L ) C3J JAX JCE , C3K KEC**  
**INT CL<sup>5</sup> C08F**

## (54) Flame retardants

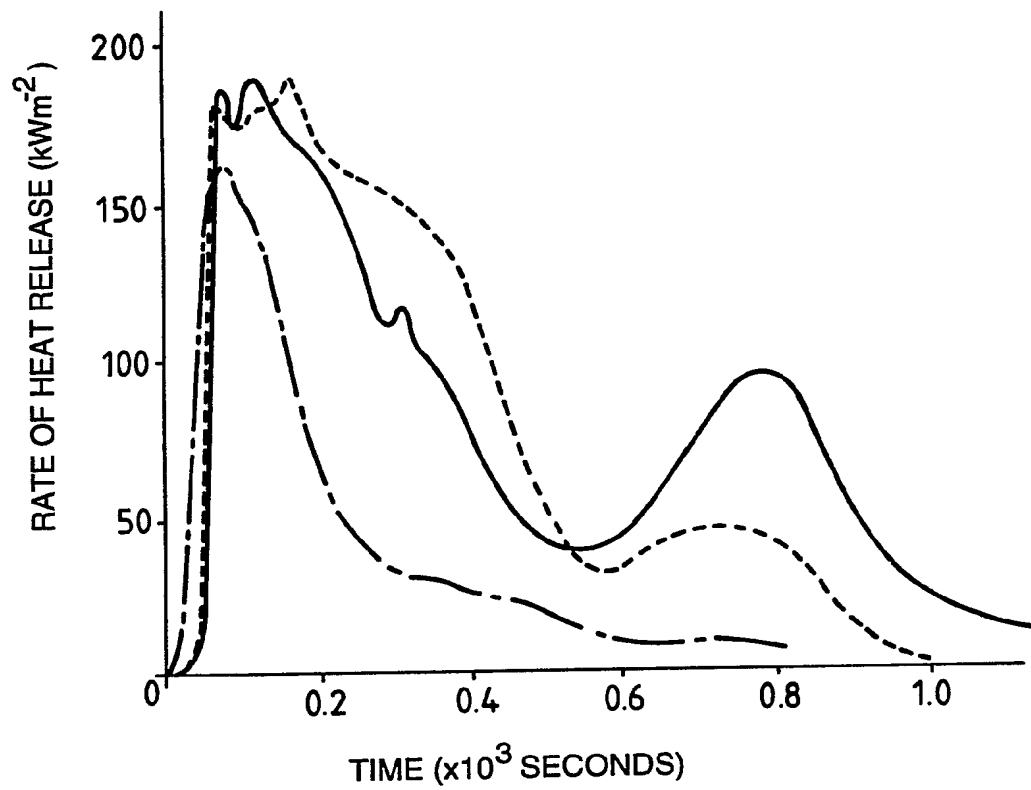
(57) A non-halogen containing flame-retardant additive comprises a salt of an inorganic phosphorus-containing acid and a polymeric compound which is a homopolymer or copolymer and comprises a linear backbone formed of at least 10 repeat units and contains a plurality of basic nitrogen functionalities. The additives may be incorporated into polymers, e.g. polyolefin polymers, or may be formulated into coating compositions.

GB 2 272 444 A

1/2

Fig.1.

COMPARATIVE FLAMMABILITY PERFORMANCE

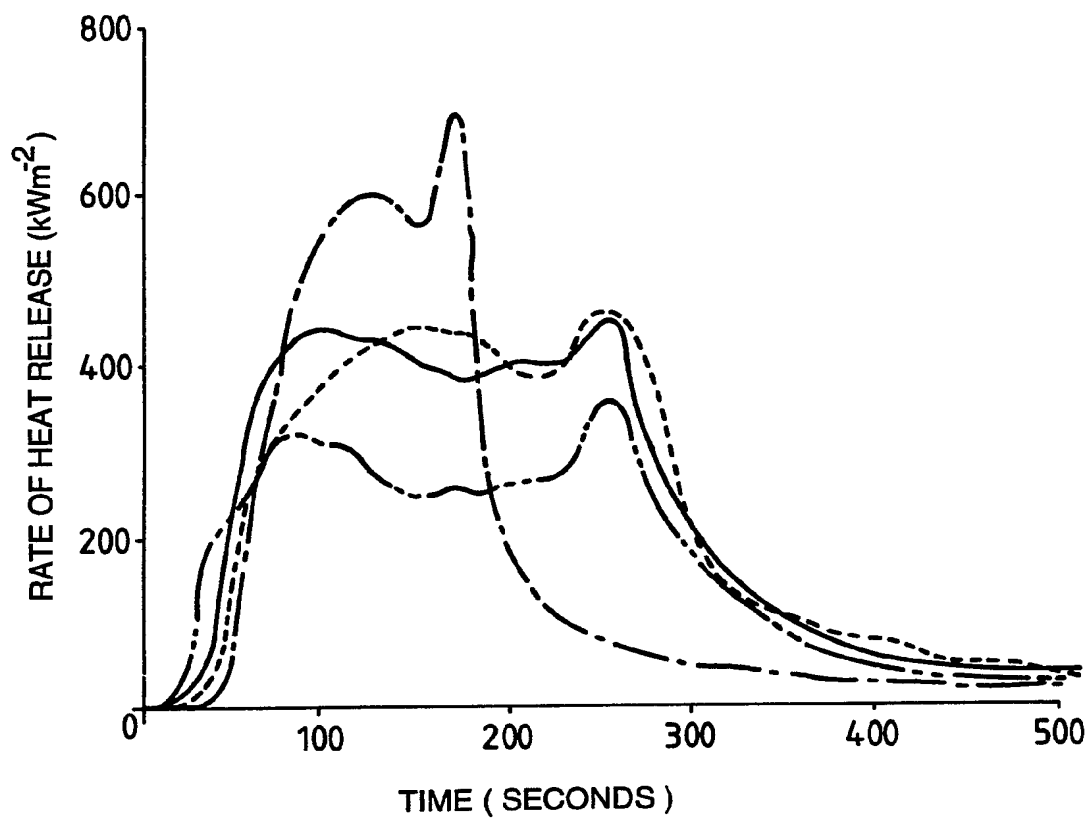


KEY

- SAMPLE 10(c) : EXOLIT IFR-23
- - - SAMPLE 11(c) : EXOLIT IFR-10
- . - SAMPLE 12 : PAP

Fig.2.

USE AS A FLAME - RETARDANT IN POLYOLEFIN / RUBBER BLENDS



## KEY

—————	SAMPLE 32(c) : EXOLIT IFR-10
-----	SAMPLE 31(c) : EXOLIT IFR-23
— · — · —	SAMPLE 33 : PAP
— · — · —	SAMPLE 34(c) : DB:ATO:ATN

FLAME RETARDANTS

This invention relates to non-halogen-containing flame-retardant additives suitable for use in a variety of thermoplastic and thermoset polymer materials.

5           Electrical fires in machinery frequently arise as a result of an electrical fault causing ignition and combustion of polymer materials, such as the insulating cladding of wires and cables. Such fires are a serious problem presenting a potential hazard to both workers and  
10           property, not only from the fire, but also from the evolution of toxic gases derived from the thermal degradation of the polymer materials. The problem may be compounded when access to the point of ignition is physically restricted, e.g., within machines, circuitry  
15           etc., thereby limiting manual attempts to extinguish or even recognise the fire. Accordingly, there has been much interest in the development of polymer compositions having improved resistance to combustion.

          It is known that blending certain compounds into  
20           a pre-polymer composition can have a flame-retarding effect on the combustion of the final product. Halogen-containing flame-retardant additives are known and have been used to reduce the flammability of polymer materials. However, there is an increasing awareness of  
25           the problems associated with the use of halogenated flame-retardants. For example, halogenated flame-retardants are known to cause both high smoke generation and the emission of toxic gases which present a hazard to both workers and fire fighters alike, as well as  
30           corrosive gases which may damage adjacent circuitry. In addition, these gases may also have wider reaching deleterious environmental effects. Alternatives to halogenated flame-retardants can be broadly classed into either (a) phosphorus-based materials or (b) non-  
35           phosphorus-based materials.

Most non-phosphorus-based materials comprise inert filler materials, such as calcium carbonate, which have little anticombustion effect. Alumina trihydrate, magnesium hydroxide and calcium carbonate have been used as flame-retardant additives for polyolefin polymers. Unfortunately, such materials require high loading by weight of the polymer composition to achieve the desired level of flammability performance. This high loading is found to have a pronounced negative effect on the physical properties of the polymer, e.g., tensile strength and/or elongation. Additionally, materials such as alumina trihydrate have poor thermal stability.

The use of phosphorus-based flame-retardants is known, particularly the use of inorganic phosphates to generate intumescent formulations which form a protective foamed char when exposed to heat, thereby preventing further combustion. Such formulations have generally found applications in cellulosic type materials, resins and formulations containing low molecular weight polyols for paints, and other such coating materials. Various phosphorus-containing compounds are disclosed in, for example: Chemical Abstracts 92 111554 and 96 143939; U.S. Patent Nos. 3485793, 3541046, 3810862, 4001177, 4140660, 4182792, 4198493, 4341694, 4433115, 4491644, 4587362, 4642366, 4742088, 5089559 and 5010133; International Patent Nos. W085/09626 and W089/01011; British Patent Nos. 2142638 and 2181141; Australian Patent Application No. 77342/87, and European Patent Publication Nos. 0026391, 0045835, 0115871, 0204027, 0413613 and 0466137. However, many of these prior art flame-retardants are found to suffer from one or more of the following disadvantages:-

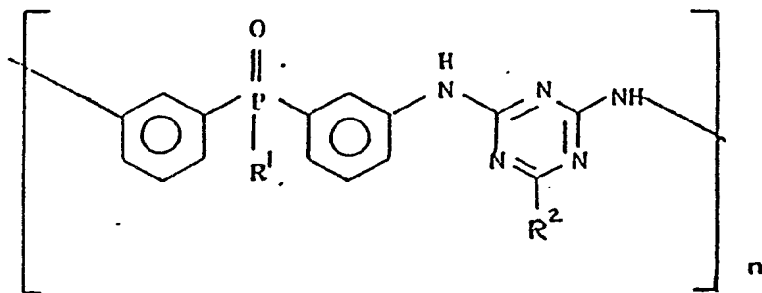
- (i) Water sensitivity.
- (ii) Migration of the additive due to non-compatibility between the component compounds and the polymer matrix.
- (iii) The deleterious action of the additive on the

physical properties of the polymer.

(iv) The high specificity of the additives.

For example, U.S. Patent No. 4491644 discloses a flame-retardant additive commercially available under the trade name CHARGARD comprising a salt formed from melamine and bis(pentaerythritol phosphate) phosphoric acid formulated for use principally in poly(propylene). Likewise, European Patent No. 0115871 discloses flame-retardant additives comprising a nitrogen-containing oligomer and ammonium polyphosphate, which are commercially available under the trade name SPINFLAM in grades specific to a particular polymer, e.g., polyethylene. Thus, there is a continuing need for a high performance method of flame-retardation for use in polymers.

Our copending European Patent Application No. 90309092.6 filed 20th August 1990 discloses a flame-retardant additive comprising a compound having a nucleus of general formula:-



in which;

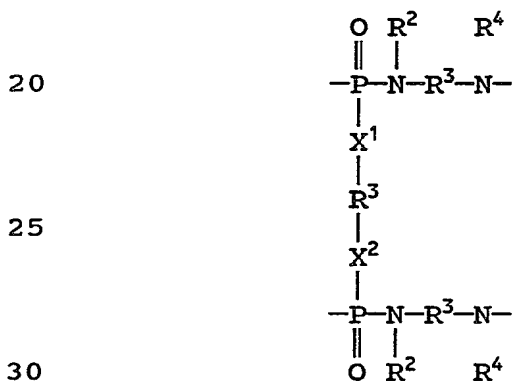
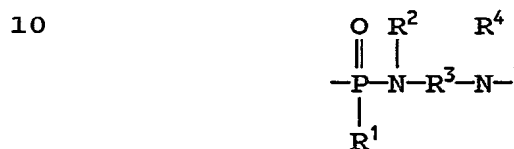
n is an integer and has a value from 2 to 25;

R¹ represents an alkyl group comprising up to 20 carbon atoms, and

R² represents R³-NH where R³ represents an alkyl group comprising up to 20 carbon atoms, an aryl nucleus comprising up to 10 carbon ring atoms, or R² represents a heterocyclic ring nucleus comprising from 4 to 8 ring

atoms, at least one ring atom being nitrogen and linking the ring nucleus to the triazine ring, optionally in combination with a source of phosphorus.

Our copending British Patent Application No. 9208926.7 filed 24th April, 1992 discloses a flame-retardant additive comprising a source of phosphorus and a polymer or oligomer having repeating units selected from those represented by general formulae:-



in which;

$\text{R}^1$  represents an alkyl group comprising up to 20 carbon atoms, an aryl group comprising up to 10 carbon ring atoms or a group represented by  $-\text{YR}^5$  where  $\text{R}^5$  is an alkyl or other aliphatic group comprising up to 20 carbon atoms or an aryl group comprising up to 10 carbon ring atoms and Y is O, S or  $-\text{NR}^6$  where  $\text{R}^6$  is a hydrogen atom, an alkyl group comprising up to 20 carbon atoms, an aryl group comprising up to 10 carbon ring atoms or  $\text{R}^5$  and  $\text{R}^6$  may together form a heterocyclic ring (including the N atom) wherein the other ring atoms are chosen from C, N, O and S;

each  $\text{R}^3$  independently represents a divalent

aliphatic linking group comprising up to 20 carbon atoms or a divalent aromatic linking group comprising up to 10 carbon ring atoms;

$R^2$  and  $R^4$  independently represent a hydrogen atom, an alkyl group comprising up to 20 carbon atoms or an aromatic group comprising up to 10 carbon ring atoms or, when  $R^3$  is aliphatic,  $R^2$  and  $R^4$  may complete a heterocyclic ring including  $-N-R^3-N-$ , the remaining ring atoms being selected from C, N, O and S, and

$X^1$  represents O, S or  $NR^2$ , where  $R^2$  is as defined previously, and

$X^2$  represents O, S or  $NR^4$ , where  $R^2$  and  $R^4$  are as defined previously.

Alternative compounds have now been found which are suitable for use in flame-retardant additives for polymer materials having reduced smoke generation, reduced evolution of corrosive gas and improved flammability properties. The compounds are compatible with a variety of polymers applicable for wire and cable insulation, heat recoverable materials and mouldable parts.

According to one aspect of the present invention there is provided a non-halogen containing flame-retardant additive comprising a salt of an inorganic phosphorus-containing acid and a polymeric compound which is a homopolymer or copolymer and comprises a linear backbone formed of at least 10 repeat units and contains a plurality of basic nitrogen functionalities. The additives are suitable for use in polymer materials either alone or in combination with other flame-retardant additives, resulting in an additive having reduced smoke generation, reduced evolution of corrosive gases and improved flame-retarding properties. The flame-retardant additives of the invention are compatible with a variety of thermoplastic and thermoset polymers applicable for wire and cable insulation, heat recoverable items, electrical tape and moulded parts. The additives may



also be formulated as a dispersion into coating compositions optionally comprising additional ingredients such as, other flame-retardants, fillers, colourants etc. In addition the additives may be employed in caulks, mastics and sealants.

According to further aspects of the present invention there is provided a polymer containing a flame-retardant loading of the additives of the invention and an article formed from such a polymer. The additives are particularly suitable for use in polymers, especially, but not exclusively, polyolefin polymers.

The polymeric compound forming the salt with the phosphorous-containing acid must possess basic nitrogen functionalities which may be present in the backbone or in groups pendant thereto. The backbone of the polymer is linear and is formed of at least 10 repeat units which need not be identical, i.e., the polymer may be a homopolymer or copolymer. The number of backbone atoms per repeat unit varies with the polymer type as is well known in the art. For example, a vinyl addition polymer has 2 backbone carbon atoms per repeat unit, while a polymer formed by a ring-opening process has x backbone atoms per repeat unit, where x is the number of atoms in the original ring. For a polymer formed by inter-reaction of two bifunctional monomers (ie a step-growth polymer), the number of backbone atoms per repeat unit is taken to be the sum of the number of catenary atoms per molecule of each of the monomers. For the purposes of this invention, polymers derived from vinyl addition or ring-opening polymerisation are preferred.

It follows that the backbone must possess at least 20 atoms exclusive of end-capping groups, and preferably it possesses at least 30 atoms. Carbon and nitrogen are the preferred backbone atoms, but other hetero-atoms such as O, S, P etc may also be present. Preferably at least 10 of the backbone atoms are selected from the group consisting of nitrogen atoms which form part of a basic

to a pendant group comprising one or more basic nitrogen functionalities. Basic nitrogen functionalities are nitrogen-containing groups which readily form salts with acids via protonation of the nitrogen. Typical examples include amines (primary, secondary or tertiary) and nitrogen-containing heterocycles such as pyridines, pyrrolidines, piperidines, morpholines etc. The term linear backbone is used to denote that the polymer possesses a recognisable backbone and is not in the form of a three-dimensional network such as those formed by urea-formaldehyde and melamine-formaldehyde condensates. Thus, the polymer may possess some branches from the backbone providing the polymer remains soluble prior to salt formation. The use of a linear backbone is advantageous in terms of ease of synthesis of the salt as it enables the use of homogenous solutions. The relatively high molecular weight of the polymers having at least 10 repeat units render the additives non-migrating and moisture insensitive in the host polymers. The salt comprises at least one unit represented by general formula (I):



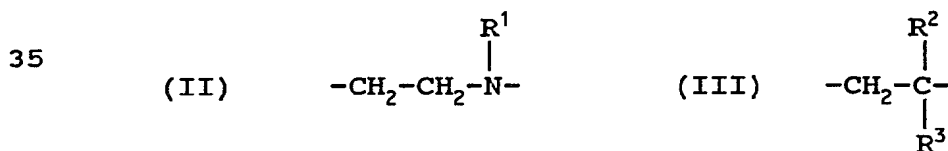
in which;

R is a nitrogen-containing repeat unit of the polymeric compound,

$X^{y-}$  is the deprotonated or partially deprotonated form of the phosphorus-containing acid, and

y is an integer. The salt preferably comprises at least ten such units and more preferably from 10 to 50 units.

R preferably represents a structure represented by general formula (II) or (III) :-

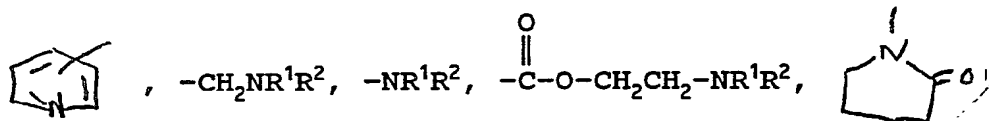


where in;

$R^1$  and  $R^2$  independently represent H or an alkyl group of up to 5 carbon atoms; and

$R^3$  represents a group comprising a basic nitrogen functionality.

5 Examples of groups represented by  $R^3$  include :-



Repeat units other than those represented by formulae II and III may also be present as a result of copolymerisation with other monomers, but this is not preferred. Examples of polymers comprising repeat units of Formula II include (but are not limited to) :  
 15 polyethyleneimine. Examples of polymers comprising repeat units of Formula III include (but are not limited to) polymers and copolymers of allylamine, 2-vinyl pyridine, 4-vinyl pyridine, 4-aminostyrene,  
 20 N,N-dimethylaminoethyl methacrylate and N-vinyl pyrrolidone. The basic nitrogen functionality may be present from the outset in the monomer(s) used to prepare the polymer (as is the case in the above examples), or may be generated by chemical conversion of precursor  
 25 groups on a preformed polymer, e.g., polyvinylamine and its N-alkyl derivatives.

Other useful polymers include the cyclopolymers derived from polymerisation of diallylamine derivatives, which comprise interlinked piperidine rings, as described  
 30 in "Encyclopaedia of Polymer Science and Engineering", 2nd Ed. Vol.4 p.543.

Examples of phosphorus-containing acids include (but are not limited to): orthophosphoric,  
 hypophosphorous, trimetaphosphoric, polyphosphoric,  
 35 phosphorous, hypophosphoric and pyrophosphoric acids.

As is well understood in this technical area, a large degree of substitution may be tolerated for groups represented by  $R^1$  to  $R^3$ . As a means of simplifying the discussion and recitation of these groups, the terms

"group", "nucleus" and "moiety" are used to differentiate between chemical species that allow for substitution or which may be substituted and those which do not or may not be so substituted. For example, the phrase "alkyl group" is intended to include not only pure hydrocarbon alkyl chains, such as methyl, ethyl, octyl, cyclo-hexyl, isooctyl, t-butyl and the like, but also alkyl chains bearing conventional non-halogen-containing substituents known in the art, such as hydroxyl, alkoxy, phenyl, nitro, amino etc. The term "nucleus" is likewise considered to allow for substitution. Thus the phrase "pyrimidine" nucleus would be understood to include not only an unsubstituted pyrimidine ring, but also pyrimidine rings bearing conventional substituents known in the art. The phrase "alkyl moiety" on the other hand is limited to the inclusion of only pure hydrocarbon alkyl chains such as methyl, ethyl, propyl, cyclohexyl, isooctyl, t-butyl and the like. Generally speaking, substituents likely to give rise to toxic fumes on combustion, such as nitrile and sulphur-containing species, are not preferred.

The flame-retardant additives may optionally be prepared by blending the P/N salts with an additional phosphorus-based flame retardant. The second phosphorus-based additive may comprise any inorganic or organic phosphorus source known in the art which (in the concentration used) does not deleteriously affect the properties of the polymer to which it is added. Preferred examples of the second phosphorus source comprise ammonium polyphosphate (commercially available under the trade name PHOSCHEK P-40 from Monsanto), melamine phosphate (commercially available under the trade name AMGARD NH from Albright and Wilson) and red phosphorus. The phosphorus source may optionally be encapsulated, e.g., in a water-insoluble resin. A preferred example is ammonium polyphosphate in melamine formaldehyde (commercially available under the trade name

EXOLIT 462 from Hoechst-Celanese).

If the P/N polymeric salt is employed in conjunction with a second phosphorus based additive, then the percentage (by weight) of the second phosphorus-based additive in the combined additive is dependent on the flammability of the polymer which is to be flame-retarded and the level of flame-retardance which is to be achieved, but preferably it is no greater than 70 percent, more preferably no greater than 50 percent and most preferably no greater than 30 percent.

The particle size of the P/N salt and the second phosphorus source is important for both flammability performance and for the physical properties of the flame-retarded material. Preferably, both additive components are in free flowing form and have an average particle size of less than 80 $\mu$ m, more preferably less than 40 $\mu$ m. Conventional methods to obtain these particle sizes include using sieves, ball milling and jet milling. Alternatively, during the preparation of the P/N compound, precipitation of the final product can be optimised to minimise particle size.

Due to the high thermal stability of the flame-retardant additive of the present invention, it is possible to impart flame-retardant properties to a wide range of polyolefins and other polymers. Preferred polymers include low density poly(ethylene) (LDPE), poly(ethylene-ethyl acrylate) (EEA), poly(ethylene-acrylic acid) (EAA), poly(ethylene-vinyl acetate) (EVA), poly(propylene) (PP), ethylene-propylene-diene monomers (EPDM) and copolymers thereof. Other preferred polymers include epoxy resins.

The choice of polymer, i.e., flammability, melt index (ASTM) and copolymer content, will affect the quantity of flame-retardant added, as will the level of flame-retardance to be achieved. Generally, the total flame-retardant loading by weight is from 10 to 60%, preferably from 20 to 50% of the total composition.

The flame-retardant additives of the invention are particularly suitable for use in EVA and EEA formulations.

5       Polymers comprising flame-retardant additives of the invention, i.e., the P/N salt(s) and optionally the second phosphorus source referred to hereinafter as the "polymers of the invention") may be cross-linked, for example, either chemically or by high energy radiation. Examples of chemical cross-linking methods include the use of free radical initiators, such as dicumyl peroxide, 10 together with co-curing agents, e.g., triallyl isocyanurate, or silane cross-linking technology, e.g., using products commercially available under the trade names MONSIL and SIOPLAS from Maillerfer and Dow Corning respectively. Cross-linking by high energy radiation can 15 also be used, for example, by irradiating with an electron beam. Radiation doses in the range 2 to 40 Mrads, preferably 10 to 20 Mrads are appropriate. To promote cross-linking during irradiation, radical 20 promoters, such as triallyl isocyanurate, can be used.

Surface treatments may be used to increase the coupling between the flame-retardant additive and the polymer host matrix. Materials such as zircoaluminates and titanates can be used or, more commonly, silane 25 coupling agents.

Other additives, for example, smoke suppressants, anti-oxidants, heat stabilisers, UV stabilisers etc., can be added. However, care must be exercised in the selection of these additives so that they do not 30 interfere with the flame-retardant mechanism of the P/N compound(s). Basic oxides, such as magnesium oxide or zinc oxide, are found to be particularly detrimental in large concentrations. Similarly, additives which contain water of hydration, e.g., alumina trihydrate, can also be 35 inhibiting in large concentrations.

Polymers incorporating the flame-retardant additives of the present invention can be processed using

conventional methods, e.g., Banbury or two-roll mill, and extruded or moulded, either by compression or injection methods. The polymer compositions of the invention are particularly suitable for use in wire and cable insulation, dimensionally recoverable products, especially heat recoverable products, moulded parts, extruded tubings, pipes and tape type constructions, where high levels of flame-retardency together with evolution of low quantities of smoke and toxic corrosive combustion products are required.

Dimensionally recoverable products are ones which by appropriate treatment can alter their dimensions. In the case of heat recoverable products, this treatment would be heat. Polymer compositions of the invention where the polymer is cross-linked EEA/EVA are particularly useful in the preparation of flexible, flame-retardant, heat recoverable tubing.

The P/N salts can be prepared by conventional procedures. For example, solutions of the nitrogen-containing polymer and the phosphorus-containing acid may be mixed in suitable proportions, causing precipitation of the desired product. Alternatively, a monomer salt may be prepared, and subjected to polymerisation by conventional methods.

The invention will now be described with reference to the accompanying, non-limiting Examples in which polymers and flame-retardant additives were compounded using a variety of methods. Polyolefin based formulations were compounded using either an electrically heated Schwabenthan two roll mill at 140°C for LDPE and 75 to 85°C for EVA and EVA/EPDM blends, or mixed using a Brabender PLASTICORDER Torque rheometer, with 30 or 300cm<sup>3</sup> internal mixing head, for 2 minutes at 100°C (EVA/EPDM) AND 140°C (LDPE). Formulation into other polymers will be discussed under the individual examples.

Test pieces were commonly produced by compression moulding using a Gem hydraulic press. Conditions

employed were 110°C for 10 minutes (EVA or EVA/EPDM) AND 150°C for 20 minutes (LDPE) with 12 ton pressure. Formulations containing other polymers will be discussed under the individual examples.

5               "EXOLIT IFR-10" and "EXOLIT IFR-23" (Hoechst-Celanese), "Epsyn 7506" (Copolymer Inc.), "LUPOLEN 1812D" (BASF), "IRGANOX 1010" and "IRGACURE651" (Ciba Geigy Chemicals), "PHOSCHEK P-30" and "PHOSCHEK P-40" (Monsanto), "EPIKOTE 815" (Shell Chemicals), "ELVAX 470" 10 (Dupont) "KR38S" (Kenrich Petrochemicals Inc.), "CN-1197" and "CHARGARD 329" (Great Lakes chemical Corporation), "SPINFLAM MF82" (Montefluos), "MONSIL" (Maillefer), "SIOPLANS" (Dow Corning), "AMGARD NH" (Albright & Wilson) and "PLASTICORDER" (Brabender) are all trade 15 names/designations.

Polymer flammability performance in the Examples was generally evaluated by two procedures, namely: the Underwriters' Laboratory UL94 vertical bar flame test and cone calorimeter performance. The latter procedure was 20 also used to determine the smoke and toxic gas production of the materials in the Examples.

Underwriter's Laboratory UL94 vertical bar flame test. This is a widely accepted test method and is commonly used by suppliers of flame-retardants and flame-retarded materials. In this test a vertically clamped 25 specimen bar is ignited by a flame from a bunsen burner. According to Part 2 of UL94, three levels of performance are defined, designated V-0, V-1 and V-2, of which V-0 is the most stringent. In the test, samples not achieving 30 V-0 and V-1 or V-2 are defined as fail. UL94 defines the specimen size as 12.7cm (5 inches) long and 1.27cm (1/2 inch) wide. The thickness of the sample must be no greater than 3.2mm (1/8 inch). UL94 performance obviously depends on specimen thickness and is generally 35 quoted for 1.6mm (1/16 inch) or 3.2mm (1/8 inch).

Cone Calorimeter Evaluation. This was generally performed in accordance with ASTM E 1354-90 and/or ISO DP



5660. In this procedure horizontally mounted specimens of dimensions 10cm x 10cm x thickness (variable dependent upon application, but 3mm in most cases) are subjected to an irradiant flux, in these Examples generally  $50\text{kWm}^{-2}$ .

5 An electric spark ignition is also provided, which is removed upon sustained burning of the specimen being observed. The fire effluent is then subject to continuous monitoring to determine a range of properties. Measurement of oxygen concentration in the gas stream as  
 10 a function of time enables the rate of heat release to be calculated as a function of time (via the oxygen consumption principle) - a key flammability property. Determination of the obscuration of a laser beam passing through the combustion product stream enables the smoke  
 15 produced to be measured, usually expressed as a specific extinction area. A variety of toxic gases can also be continuously monitored, in particular carbon monoxide, carbon dioxide and oxides of nitrogen, the first two by means of infrared spectroscopy and the latter by means of  
 20 a chemiluminescence detector. Additionally the test specimen is mounted on a load cell throughout the test so that all the measured properties can be related to a rate of mass loss. Important abbreviations used for cone calorimeter data are as follows;

25           RHR    = Rate of Heat Release (in  $\text{kWm}^{-2}$ ),  
            $t_{ig}$     = Time to ignition (in s),  
           EHC    = Effective Heat of combustion (in  $\text{MJkg}^{-1}$ ),  
           SEA    = specific Extinction area (in  $\text{m}^2\text{kg}^{-1}$ ),  
           SPR    = Smoke Production rate (in  $\text{s}^{-1}$ ),  
 30           COPR   = Carbon Monoxide Production Rate  
                   (in  $\text{kgm}^{-2}\text{s}^{-1}$ ),  
           NOx    = Nitrogen Oxides Yield (in  $\text{kgkg}^{-1}$ ),

          RHR can be visualised as the intensity of the fire, so the lower the values of RHR the better in terms  
 35 of flammability performance. SEA is a widely used smoke performance parameter relating the amount of smoke produced to the mass loss rate of the burning specimen.

The terms SPR and COPR are defined by  $SPR = SEAxRHR/EHC$  and  $COPR = COxRHR/EHC$ . In all cases it is desirable for the values of these properties to be as low as possible.

Physical properties were determined using an  
 5 Instron Model 1026, employing a crosshead speed of 500mm min<sup>-1</sup>.

#### EXAMPLE 1.

##### PREPARATION OF POLY(ALLYLAMMONIUM) PYROPHOSPHATE

poly(allylammonium hydrochloride) (120.00g;  
 10 1.27mol) (supplied by Nitto Boseki Co. Ltd under the designation PAA-HCL-105) was treated with a small excess of sodium hydroxide (65.00g; 1.63mol) in methanol (2500 ml) and refluxed for 18 hours under dry conditions. On  
 15 cooling the solution was filtered to remove sodium chloride. The remaining solution was reduced in volume to ca. 800ml and further sodium chloride removed. A portion of this solution (250ml; ca.0.40 mol polyallylamine) was diluted to 800ml with methanol. The  
 20 resulting solution was then stirred vigorously while a concentrated methanolic solution of pyrophosphoric acid (30.00g/140ml; 0.17mol) was added until pH 7 (neutrality) was reached. The copious white solid (solvent swollen) produced was filtered, washed with methanol (4x100ml) and dried in vacuo at 160°C for 18 hours. Yeild=57.00g  
 25 (98%). The product is insoluble in water.

Thermal analysis of the product reveals 1 to 2% of volatiles even after prolonged drying. Thermogravimetric analysis (TGA) in air reveals the compound is stable up to ca. 200°C. Ca. 50% weight of  
 30 residue is retained up to 740°C.

Chemical analysis of the product revealed:  
 N=8.29% and P=18.29% with a N/P ratio of 1:1.004  
 [Theoretical: N=9.59% and P=21.20% with N/P ratio of 1:1]

#### EXAMPLE 2

##### ALTERNATIVE PREPARATION OF POLY(ALLYAMMONIUM) PYROPHOSPHATE

This Example illustrates an alternative procedure

for the preparation of poly(allylammonium) pyrophosphate. The procedure is as disclosed in European Patent Publication No. 145220.

5 A 500ml flange flask was fitted with a condenser, a mechanical stirrer and a nitrogen inlet. Pyrophosphoric acid (89.000g, 0.500mol) was dissolved in 30ml of distilled water with cooling. The acidic solution was ice cooled to ensure that the temperature did not exceed 20°C upon dropwise addition of allylamine (37.500ml: 10 0.500mol). The addition was performed with stirring under a dry nitrogen atmosphere. The resulting solution was treated with a warm (50°C) aqueous solution of 2,2'-azobis[2-amidinopropane] (1.000g in water (10ml)) and stirred for 24 hours at 60°C. The viscous product was 15 washed with water repeatedly in a blender until nothing further dissolved. The product was then dried in vacuo at 110°C for 18 hours on siliconised (lubricated/non-stick) paper. Yield = 58.6g.

### EXAMPLE 3

#### 20 OPTIMISATION OF POLY(ALLYLAMMONIUM) PYROPHOSPHATE FLAMMABILITY PERFORMANCE - UL94 TESTING.

Phosphorus/nitrogen-containing flame-retardants conventionally comprise three active components, namely: an acid source; a char former and a spumific or blowing 25 agent. In some cases there may be only two active components, e.g., ammonium polyphosphate (APP) with trishydroxyethyl isocyanurate (THEIC).

Since the compounds of the invention could be envisaged as fulfilling the role of APP in a flame- 30 retardant system, then it may be thought that they should be employed in the presence of a char former, such as THEIC. Different ratios of poly(allylammonium) pyrophosphate:THEIC were examined in order to investigate the flammability performance in non-cross-linked EVA 35 (ELVAX 470; Dupont). The results obtained are reported in TABLE 1.

TABLE 1

Sample	Additive	Loading (%)	UL-94 Tests (0.16cm)	Observations
1	PAP:THEIC[1:1]	40	Fail	2nd Ignition
2	PAP:THEIC[7:5]	40	Fail	2nd Ignition
3	PAP:THEIC[2:1]	40	Fail	2nd Ignition
4	PAP:THEIC[3:1]	40	V-0	6 second flaming time
5	PAP:THEIC[5:1]	40	V-0	3 second flaming time
6	PAP	40	V-0	No flaming time

Unexpectedly, optimum performance was seen when poly(allylammonium) pyrophosphate was used alone.

EXAMPLE 4COMPARATIVE FLAMMABILITY PERFORMANCE - UL94 TESTING.

This Example compares the flammability performance of poly(allylammonium) pyrophosphate with known phosphorus/nitrogen-containing flame-retardants: The comparative systems were: EXOLIT IFR-10 (Hoechst Celanese) and ammonium polyphosphate (APP) (PHOSCHEK P-40, Monsanto). The results obtained are shown in TABLE 2. All data refer to samples in non-crosslinked EVA (ELVAX 470).

TABLE 2

Sample*	Additive	UL-94 Tests (0.16cm)	Observations
7	PAP	V-0	No flaming time
8(c)	APP	Fail	2nd Ignition
9(c)	EXOLIT IFR-10	V-0	2 second flaming time

\* (c) = comparative sample not in accordance with the invention.

The results suggest poly(allylammonium) pyrophosphate is a better performer than either of the known phosphorus/nitrogen-containing flame-retardants, with no flaming time observed in attaining its UL94 V-0 rating.

EXAMPLE 5Comparative Flammability Performance - Cone Calorimeter Testing.

This Example demonstrates the flammability performance of poly(allylammonium) pyrophosphate when compared with known phosphorus/nitrogen-containing flame-retardants. The comparative systems were: EXOLIT IFR-10 and EXOLIT IFR-23 (Hoechst-Celanese). All data refers to samples in non-crosslinked EVA ELVAX 470). A standard irradiant flux level of  $50\text{kWm}^{-2}$  was employed. Two runs were undertaken for each sample and the results were averaged. The results obtained are reported in TABLE 3.

TABLE 3

Sample*	Additive	Loading (t)	RHR ( $\text{kWm}^{-2}$ )		SEA ( $\text{m}^2\text{kg}^{-1}$ )		SPR ( $\text{s}^{-1}$ )		COPR ( $10^4\text{kgm}^{-2}\text{s}^{-1}$ )	
			Peak	Average	Peak	Average	Peak	Average	Peak	Average
10(c)	EXOLIT IFR-23	40	185	80	847	466	3.92	1.37	2.59	0.65
11(c)	EXOLIT IFR-10	40	186	77	635	361	3.94	1.15	2.66	0.76
12	PAP	40	154	50	834	423	3.88	0.95	2.63	0.61

\* (c) = comparative sample not in accordance with the present invention.

These results show that poly(allylammonium) pyrophosphate performs excellently as a flame retardant, being generally at least as good as the state-of-art commercial materials and noticeably better with regard to the key parameter: RHR. FIGURE 1 shows dramatically the improvement in RHR realised by utilising poly(allylammonium) pyrophosphate as opposed to both EXOLIT IFR-10 and IFR-23. Poly(allylammonium) pyrophosphate produces a better protective char for unburned fuel than either EXOLIT IFR-10 or EXOLIT IFR-23 as evidenced by the lack of a second period of heat release up to nearly 800 seconds. Evidence of this is that upon completion of the test and removal of the sample holder assembly from the apparatus, a considerable amount of molten, unburned material is visible under the char. Poly(allylammonium) pyrophosphate test pieces also show a much lower mass loss rate during the test.

EXAMPLE 6SURFACE TREATMENT

This Example demonstrates the usefulness of surface treatment of the P/N polymeric salts to improve their dispersibility in polymers and hence the physical properties of the resulting material. A number of surface treatment agents can be used, including titanates, silanes, zirconates and zircoaluminates, but the particular example chosen here is the titanate commercially available from Kenrich Petrochemicals Inc. Under the trade designation KR38S. The flame-retardant, in this case poly(allylammonium) pyrophosphate, was ball milled for 16 hours in a 2% w/w solution of KR38S in toluene (concentrations of between 0.5% and 5.0% could be used), resulting in a fine, easily dispersable powder. The particle size can be reduced further by jet milling if necessary.

This surface treatment procedure enhances the dispersability of only these types of phosphorus/nitrogen compounds, not all P/N compounds, as illustrated by the corresponding data for ammonium polyphosphate PHOSCHEK P-40. The physical/mechanical property results below apply to a polyolefin/rubber blend of EVA (ELVAX 470: melt index 0.7; vinyl acetate content 18%) : EPDM (EPsyn 7506; Copolymer Inc.) (4:1). The particle size of the titanate treated and untreated poly(allylammonium) pyrophosphate was less than 53 $\mu$ m in both cases, whereas the ammonium polyphosphate has an average particle size of 10 $\mu$ m in each case. The results obtained for poly(allylammonium) pyrophosphate and ammonium polyphosphate are reported in TABLE 4 below.

TABLE 4

Sample	Additive	Loading (%)	Surface Treated	Tensile Strength at break Nm <sup>-2</sup>	Elongation at break (%)
13	PAP	26	YES	1.441x10 <sup>7</sup> (2089psi)	838
14	PAP	26	NO	9.535x10 <sup>7</sup> (1383psi)	690
15(c)	APP	26	YES	1.291x10 <sup>7</sup> (1873psi)	921
16(c)	APP	26	NO	1.257x10 <sup>7</sup> (1823psi)	983

\* (c) = comparative sample not in accordance with the present invention.

EXAMPLE 7USE IN COMBINATION WITH AMMONIUM POLYPHOSPHATE

This Example demonstrates that the P/N polymeric salts can be used in combination with other sources of phosphorus without deleterious consequences, and in some cases with improvement upon, flammability properties. The examples quoted below are all KR38S titanate surface treatment poly(allylammonium) pyrophosphate (PAP) of particle size less than  $53\mu\text{m}$ , compounded in (EVA ELVAX 470:EPDM EPsyn 7506) [4:1] (as per EXAMPLE 6). Cone calorimeter data was obtained at  $50\text{kWm}^{-2}$  irradiant flux. The results obtained are shown in TABLE 5

TABLE 5

Sample	Additive	Loading (%)	Surface Treated	$t_{ig}(s)$	$\backslash$ RHR ( $\text{kWm}^{-2}$ )		SEA ( $\text{m}^2\text{kg}^{-1}$ )		CO ( $\text{kgkg}^{-1}$ )		NO <sub>x</sub> ( $\text{kgkg}^{-1}$ )	
					peak	av.	peak	av.	peak	av.	peak	av.
17	PAP	26	YES	36	280	98	824	601	0.07	0.04	0.009	0.006
18	PAP	26	NO	17	226	92	925	785	0.08	0.06	0.009	0.006
19	PAP:APP [9:1]	26	YES	34	260	112	715	549	0.07	0.05	0.007	0.006
20	PAP:APP [4:1]	26	YES	29	211	86	721	421	0.07	0.05	0.007	0.006
21	PAP:APP [7:3]	26	YES	28	241	116	753	622	0.08	0.05	0.006	0.005

EXAMPLE 8

USEFULNESS OF PAP TREATED WITH VARIOUS COUPLING AGENTS  
WITH A SECOND PHOSPHORUS SOURCE.

This example demonstrates the performance of PAP with a variety of titanate and silane coupling agents, with or without the addition of a second phosphorus source, namely ammonium polyphosphate PHOSCHEK P-40). All materials were evaluated in EVA EPsyn [4:1] in terms of cone calorimeter performance. Coupling agents used were KR38S titanate (Kenrich Petrochemicals Inc.), 3-aminopropyltrimethoxysilane and amyltriethoxysilane. A sample containing ammonium polyphosphate as the flame-retardant is included for comparison. All cone calorimeter experiments were performed at  $50\text{kWm}^{-2}$  irradiant flux and all PAP samples were reduced to a

particle size of less than  $53\mu\text{m}$ . The results obtained are shown in TABLE 6.

TABLE 6

Sample	Additive	Loading (%)	Coupling Agent	$t_{ig}$ (s)	RHR ( $\text{kWm}^{-2}$ )		SEA ( $\text{m}^2\text{kg}^{-1}$ )		CO ( $\text{kgkg}^{-1}$ )	
					peak	av.	peak	av.	peak	av.
22	PAP	26	titanate	21	280	98	824	601	0.07	0.04
23	PAP:APP[4:1]	26	titanate	31	211	86	721	421	0.07	0.05
24	PAP	26	amino silane	23	221	81	696	507	0.08	0.06
25	PAP:APP[4:1]	26	amino silane	23	205	69	751	471	0.07	0.06
26	PAP	26	amyl silane	29	202	95	751	544	0.09	0.06
27	PAP:APP[4:1]	26	amyl silane	23	196	84	778	575	0.08	0.05
28(c)	APP	26	-	50	519	178	914	659	0.04	0.03

\* (c) = sample not in accordance with the invention.

## EXAMPLE 9

## SHELF LIFE TESTING

A three month old sample of PAP (KR38S titanate treated) was blended with ammonium polyphosphate (PHOSCHEK P-40) [4:1] and compounded into EVA (ELVAX 470):EPDM(EPsyn 7506) [4:1] at a 26% loading level. The flammability data for this sample and that of an analogous one containing a freshly prepared batch of the same flame retardants are shown below. In both cases the data was derived from the cone calorimeter. The heat flux was  $50\text{KWm}^{-2}$  for both materials. The results obtained are shown in TABLE 7.

TABLE 7

Sample	Additive	Loading (%)	$t_{ig}$ (s)	RHR ( $\text{kWm}^{-2}$ )		SEA ( $\text{m}^2\text{kg}^{-1}$ )		CO ( $\text{kgkg}^{-1}$ )		NO <sub>x</sub> ( $\text{kgkg}^{-1}$ )	
				peak	av.	peak	av.	peak	av.	peak	av.
29 (fresh)	PAP:APP [4:1]	26	31	289	113	682	549	0.07	0.05	0.005	0.006
30 (aged)	PAP:APP [4:1]	26	32	245	89	731	544	0.08	0.06	0.007	0.005

## EXAMPLE 10

## USE AS A FLAME RETARDANT IN POLYOLEFIN/RUBBER BLENDS

The flammability performance of PAP alone is



compared below with the state-of-the-art commercial non-halogen flame-retardants EXOLIT IFR-10 and EXOLIT IFR-23 and a typical halogenated flame-retardant based on the following commercially available materials -

5 decabromodiphenyloxide (DB): antimony oxide (ATO): alumina trihydrate (ATH) (2:1:1). DB was obtained from Great lakes Chemicals, ATO from Anzon America Inc. (11-0000-2556-6) and ATH is the 932 grade from Solem. All cone calorimeter data refer to non-cross-linked EVA  
10 (ELVAX 470): EPDM (EPSyn 7506) [4:1]. As in the previous examples a standard irradiance level of  $50\text{kW}^2$  was employed. Again two runs were undertaken for each sample and the results averaged. The results obtained are shown in TABLE 8 and Figure 2 of the accompanying drawings.

15 TABLE 8

Sample*	Additive	Loading (%)	RHR ( $\text{kWm}^{-2}$ )		SPR(s)		COPR ( $10^4\text{kgm}^{-2}\text{s}^{-1}$ )	
			Peak	Average	Peak	Average	Peak	Average
31(c)	EXOLIT IFR-23	20	431	238	8.87	4.85	6.66	3.66
32(c)	EXOLIT IFR-10	20	497	255	10.3	5.03	5.51	3.01
33	PAP	20	346	181	8.52	4.32	5.51	2.91
34(c)	DB:ATO:ATH	20	674	196	29.70	7.98	33.05	10.30

\* (c) = comparative sample not in accordance with the invention.

EXAMPLE 11

USE AS FLAME RETARDANT IN EPOXY RESINS

25 This Example demonstrates the utility of PAP used either alone or in conjunction with PHOSCHEK P-40 ammonium polyphosphate PHOSCHEK P-40, as a flame-retardant for thermoset epoxy resins. The particular  
30 example here consists of a resin based upon 2 parts of EPIKOTE 815 (Shell Chemicals) cured with 1 part 2,4,6-dimethylaminomethylphenol, containing between 20 and 30% of flame-retardant. Specimens were cured at  $110^\circ\text{C}$  for 16 hours and then evaluated on a cone  
35 calorimeter at  $50\text{kWm}^{-2}$  irradiant flux. In all cases here PAP was surface treated with 3-aminopropyltrimethoxysilane and its particle size was

less than  $53\mu\text{m}$ . The results obtained are shown in TABLE 9.

TABLE 9

Sample	Additive	Loading (%)	$t_{ig}(s)$	RHR ( $\text{kWm}^{-2}$ )	
				peak	av.
CONTROL	-	-	40	814	132
35	PAP	20	42	302	103
36	PAP	30	40	268	80
37(c)	APP	20	33	241	75
38	PAP:APP [1:2]	20	32	238	83
39	PAP:APP [1:1]	20	52	250	89
40	PAP:APP [2:1]	20	42	250	94

\* (c) = sample not in accordance with the present invention.

## EXAMPLE 12

USE AS A FLAME RETARDANT IN LOW DENSITY POLYETHYLENE.

This Example demonstrates the usefulness of compounds of general formula (1), with or without a second phosphorus source, as flame retardants for low density polyethylene. Formulations were prepared in the aforementioned fashion and evaluated on a cone calorimeter at an irradiant flux of  $50\text{kWm}^{-2}$ . Formulation constituents were as shown in TABLE 10 in which the following nomenclature is employed:.

TABLE 10

Sample*	Constituent (%)						
	LDPE	DBDPO	ATO	IRGANOX 1010	Stearic Acid	PAP	PHOSCHEK P-40
45(c)	68.3	25.0	5.0	0.7	1.0	-	-
46	68.3	-	-	0.7	1.0	30.0	-
47	68.3	-	-	0.7	1.0	24.0	6.0

\* (c) = sample not in accordance with the present invention.

LDPE = LUPOLEN 1812 D,

DBDPO = decabromodiphenyl oxide (Great Lakes Chemical Corp.),

ATO = antimony trioxide (Anzon America Inc.),

IRGANOX 1010 = Ciba Geigy Chemicals,  
 Stearic Acid = Aldrich Chemical Company Ltd,  
 PHOSCHEK P40 = ammonium polyphosphate (Monsanto),  
 PAP = poly(allylammonium) pyrophosphate.

Cone calorimeter evaluation produced the results shown in  
 TABLE 11.

TABLE 11

Sample*	Additive	Loading (%)	RHR(kWm <sup>-2</sup> )		SEA(m <sup>2</sup> kg <sup>-1</sup> )	CO(kgkg <sup>-1</sup> )
			peak	av.	av.	av.
45(c)	DBDPO:ATO [5:1]	30	495	92	1284	0.112
46	PAP	30	169	91	748	0.061
47	PAP:APP [4:1]	30	170	96	655	0.054

\* (c) = sample not in accordance with the present invention.

It will be noted the compounds of this invention,  
 whether used alone or in conjunction with a second  
 phosphorus source, confer excellent properties upon LDPE  
 in terms of rate of heat release, smoke generation and  
 toxic gas yield, considerably outperforming a widely used  
 flame retardant additive system such as decabromodiphenyl  
 oxide/antimony trioxide.

#### EXAMPLE 13

##### USE AS A FLAME RETARDANT IN CROSS-LINKED POLYOLEFINS

This Example demonstrates the usefulness of PAP,  
 as a 4:1 blend with ammonium polyphosphate PHOSCHEK P-40,  
 in crosslinked ethylene-vinyl acetate copolymer (ELVAX  
 470). Formulations were prepared containing either 45%  
 or 50% total flame retardant plus 3% trimethylolpropyl  
 trimethacrylate electron beam prorad and 1 phr stearic  
 acid. These materials were extruded into tubing of  
 outside diameter 0.64cm (0.25 inches) and wall thickness  
 25μm (25mils), which was then cross-linked by means of  
 exposure to an electron beam dose of 10MRad.

Flammability performance was assessed by means of  
 the Underwriters' Laboratories UL224 test for tubing

materials. This involves the application of a Bunsen Flame to the vertically clamped tubing for five 15 second burns, each separated by an interval of either 15 seconds or the observed flaming time of the specimen, whichever is greater. For the specimen to attain the required pass rating, termed VW-1, the flaming time in each case must not exceed 60 seconds and the material must emit no flaming drips which ignite a cotton wool pad placed underneath the specimen. Each material is generally tested five times, and if any specimen does not meet the pass criteria it is deemed to be not VW-1 rated. It has also been found useful, although not part of the UL224 specification, to classify materials by means of an average flame number 'F' which represents the total flaming time observed for a specimen, i.e., the sum of the flaming times for each bunsen application. The lower the value of F the better is the material in terms of its flammability performance. The results obtained are shown in TABLE 12.

TABLE 12

Sample*	Additive	Loading (%)	UL224 Rating	Average F(s)
48	PAP:APP [4:1]	45	VW-1	2
49	PAP:APP [4:1]	50	VW-1	8
50(c)	EXOLIT IFR-10	45	VW-1	30
51(c)	EXOLIT IFR-10	50	VW-1	17
52(c)	EXOLIT IFR-23	45	not VW-1	69
53(c)	EXOLIT IFR-23	50	VW-1	30

\* (c) = not in accordance with comparative sample in invention.

The PAP used to demonstrate this example was surface treated with N-(3-acryloxy-2-hydroxypropyl)-3-aminopropyl triethoxysilane and was of particle size less than 53 $\mu$ m. Comparative materials quoted are EXOLIT IFR-10 and EXOLIT IFR-23.

Hence the blend of PAP with [4:1] outperforms

both EXOLIT IFR-23 at either 45% or 50% loading in the cross-linked polyolefin of this example.

#### EXAMPLE 14

#### DEMONSTRATION OF A RANGE OF NITROGEN CONTAINING POLYMERS PERTAINING TO THIS INVENTION.

This Example demonstrates the performance of variety of P/N polymeric salts in addition to the erstwhile demonstrated examples regarding poly(allylammonium) as the polymeric cation in the salt. All flame retardants were evaluated as single additives, with no secondary phosphorus source, in a polyolefin/rubber blend consisting of EVA (ELVAX 470):EPDM(EPsyn 7506) [4:1], non cross-linked, at a loading of 26%. Cone calorimeter evaluation was carried out at an irradiant flux of 50kWm<sup>-2</sup>. Materials examined were poly(allylammonium) pyrophosphate surface treated with KR38S titanate [I], poly(ethyleneiminium) pyrophosphate [II], poly(2-vinylpyridinium) pyrophosphate [III], poly(1-vinylpyrrolidonium) pyrophosphate [IV], poly(N-[2-(methacryloyl)ethyl]-N,N-dimethylammonium) orthophosphate (V) poly(N-methylvinylammonium) pyrophosphate [VI] and poly(4-styrylammonium) pyrophosphate [VII]. Comparative data is also given for the phosphorus nitrogen flame retardant CN-1197 (Great Lakes Chemical Corp.) The results obtained are shown in TABLE 13.

TABLE 13

Sample	Additive	Loading (%)	t <sub>ig</sub> (s)	RHR (kWm <sup>-2</sup> )		SEA (m2kg <sup>-1</sup> )		CO (kgkg <sup>-1</sup> )		NO <sub>x</sub> (kgkg <sup>-1</sup> )
				peak	av.	peak	av.	peak	av.	av.
54	[I]	26	21	267	127	1000	549	0.08	0.05	-
55	[II]	26	22	231	97	684	497	0.06	0.04	-
56	[III]	26	23	375	165	1093	801	0.07	0.06	-
57	[IV]	26	23	376	153	1061	746	0.08	0.07	-
58	[V]	26	29	497	164	1016	715	0.06	0.06	-
59	[VI]	26	21	226	102	812	608	0.06	0.06	0.0066
60	[VII]	26	31	392	133	1146	790	0.08	0.07	0.0051
60(c)	CN-1197	26	20	445	179	1050	745	0.06	0.05	0.0070

The results demonstrate that a range of polymeric salts of the invention show excellent flammability properties, smoke production and toxic gas production characteristics.

5

#### EXAMPLE 15

#### DEMONSTRATION OF A RANGE OF PHOSPHORUS CONTAINING ACIDS PERTAINING TO THIS INVENTION

This Example demonstrates the usefulness of a range of phosphorus containing acids that could be considered for compounds of general formula(I). Salts examined here are poly(allylammonium) pyrophosphate [VIII], poly(allylammonium) polyphosphate [IX], poly(allylammonium) orthophosphate [X] and poly(allylammonium) hypophosphite [XI]. None of these materials were subject to surface treatment and all were used without recourse to a second phosphorus source. [VIII] and [IX] were evaluated at a loading of 40% in ethylene-vinyl acetate copolymer (EVA, ELVAX 470, Dupont). [VIII], [X] and [XI] were evaluated at a loading of 26% in EVA(ELVAX 470):EPDM(EPsyn 7506) [4:1]. Cone calorimeter performance was evaluated at an irradiant flux of  $50\text{kWm}^{-2}$ . The results obtained for Additives VIII and IX in EVA and additives VIII to XI in EVA:EPDM[4:1] are shown in TABLES 14 and 15, respectively.

25

TABLE 14

Sample	Additive	Loading (%)	RHR ( $\text{kWm}^{-2}$ )		SEA ( $\text{m}^2\text{kg}^{-1}$ )	
			peak	av.	peak	av.
62	[VIII]	26	154	50	831	423
63	[IX]	26	180	77	883	608
64	EXOLIT IFR-23	26	185	80	847	466

30

35

TABLE 15

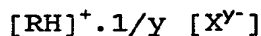
Sample	Additive	Loading ( $\frac{\text{g}}{\text{s}}$ )	$t_{ig}(s)$	RHR ( $\text{kWm}^{-2}$ )		SEA ( $\text{m}^2\text{kg}^{-1}$ )		CO ( $\text{kgkg}^{-1}$ )		NO <sub>x</sub> ( $\text{Kgkg}^{-1}$ )	
				peak	av.	peak	av.	peak	av.	peak	av.
65	(VIII)	26	17	226	92	925	785	0.08	0.06	0.009	0.006
66	(X)	26	28	267	109	882	696	0.08	0.06	0.008	0.006
67	(XI)	26	39	284	112	1030	797	0.13	0.10	0.009	0.006

CLAIMS:

5 1. A non-halogen containing flame-retardant additive comprising a salt of an inorganic phosphorus-containing acid and a polymeric compound which is a homopolymer or copolymer and comprises a linear backbone formed of at least 10 repeat units and contains a  
10 plurality of basic nitrogen functionalities.

2. A flame-retardant additive as claimed in Claim 1 in which the backbone of the polymer and/or groups pendant thereto contain a primary, secondary or tertiary amino group.

15 3. A flame-retardant additive as claimed in Claim 1 or Claim 2 in which the salt comprises a plurality of units represented by general formula:



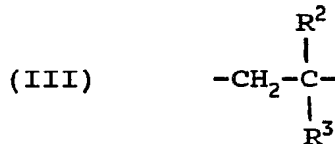
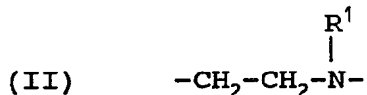
in which;

20 R is a nitrogen-containing repeat unit of the polymeric compound;

$\text{X}^{y-}$  is the deprotonated or partially deprotonated form of the phosphorus-containing acid, and Y is an integer.

25 4. A flame-retardant additive as claimed in Claim 3 in which the salt comprises from 10 to 50 of said units.

5. A flame-retardant additive as claimed in claim 3 or Claim 4 in which R represents a structure  
30 represented by general formula (II) to (III)



35 in which;

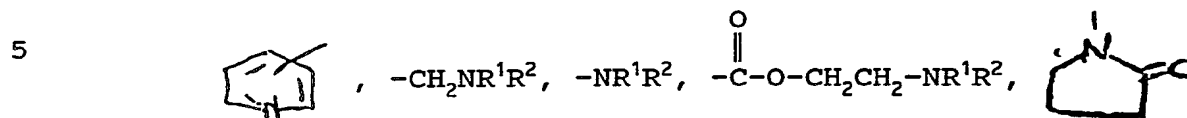
$\text{R}^1$  and  $\text{R}^2$  independently represent H or an alkyl group of up to 5 carbon atoms; and

40  $\text{R}^3$  represents a group comprising a basic



nitrogen functionality.

6. A flame-retardant additive as claimed in claim 5 in which  $R^3$  is selected from



10 n which;

$R^1$  and  $R^2$  are as defined in Claim 5.

7. A flame-retardant additive as claimed in Claim 5 or Claim 6 in which the polymer is a polymer or copolymer of allylamine, ethyleneimine, 2-vinyl pyridine, 4-vinyl pyridine, 4-aminostyrene, N,N-dimethylaminoethyl methacrylate and N-vinyl pyrrolidone.

8. A flame-retardant additive as claimed in any preceding Claim in which the phosphorus-containing acid is orthophosphoric acid, polyphosphoric acid, hypophosphorus acid, trimetaphosphoric acid, phosphinic acid, phosphorous acid, hypophosphoric acid, or pyrophosphoric acid.

9. A flame-retardant additive as claimed in any preceding Claim further comprising a second source of phosphorus different from said salt.

10. A flame-retardant additive as claimed in Claim 9 in which the second source of phosphorus comprises ammonium polyphosphate, melamine polyphosphate or red phosphorus.

11. A flame-retardant additive as claimed in Claim 9 or Claim 10 in which the second source of phosphorus is encapsulated in a water-insoluble resin.

12. A flame-retardant additive as claimed in any one of Claims 9 to 11 in which the second source of phosphorus comprises not more than 70% by weight of the additive.

13. A flame-retardant additive as claimed in Claim 12 in which the second source of phosphorus comprises not more than 50% by weight of the additive.

14. A flame-retardant additive as claimed in Claim 13 in which the second source of phosphorus comprises not more than 30% by weight of the additive.

5 15. A flame-retardant additive as claimed in any preceding Claim in which the salt and/or the second source of phosphorus are prepared as dry, free flowing particles having an average particle size of less than 80 $\mu$ m.

10 16. A flame-retardant additive as claimed in Claim 15 in which the salt and/or the second source of phosphorus are prepared as particles having an average particle size of less than 40 $\mu$ m.

17. A flame-retardant additive as claimed in any preceding Claim which has been surface treated.

15 18. A flame-retardant additive as claimed in Claim 17 which has been surface treated with a material selected from zircoaluminates, titanates and silane coupling agents.

20 19. A flame-retardant additive as claimed in Claim 1 substantially as herein described with reference to any of the accompanying Examples.

25 20. A product comprising a flame-retardant additive as claimed in any one of Claims 1 to 19 in combination with information or instructions for the use of the same as a flame-retardant additive.

30 21. A method of imparting flame-retarding properties to a polymeric product which comprises adding to the prepolymer composition of the product a flame-retardant loading of a flame-retardant additive as claimed in any one of Claims 1 to 19.

22. A polymer having a flame-retardant loading of a flame-retardant additive as claimed in any one of Claims 1 to 19.

35 23. A polymer as claimed in Claim 22 in which the flame-retardant additive is present in an amount of from 10 to 60% by weight of the polymer.

24. A polymer as claimed in Claim 23 in which the flame-retardant additive is present in an amount of from 20 to 50% by weight of the polymer.

5 25. A polymer as claimed in any one of Claims 22 to 24 in which the polymer is a homopolymer or copolymer of an olefin, an acrylate or an epoxy resin.

10 26. A polymer as claimed in Claim 25 in which the polymer is low density poly(ethylene), high density poly(ethylene), linear low density poly(ethylene), poly(ethylene/acrylic acid), poly(ethylene/ethyl acrylate), poly(ethylene/vinyl acetate), poly(propylene) or ethylene-propylene/vinyl acetate, poly(propylene) or ethylene-propylene-diene monomers.

15 27. A polymer as claimed in any one of Claims 22 to 26 in which the polymer is cross-linked.

28. A polymer as claimed in Claim 27 in which the polymer is cross-linked chemically or by means of high energy radiation.

20 29. A polymer as claimed in Claim 22 substantially as herein described with reference to any of the accompanying Examples.

30. An article formed from a polymer as claimed in any one of Claims 22 to 29.

25 31. An article as claimed in Claim 30 in the form of a tube, pipe, sheet, tape or other moulded article.

32. An article as claimed in Claim 30 in the form of a caulk, mastic or sealant.

30 33. An article as claimed in Claim 30 substantially as herein described.

34. A coating composition comprising a dispersion of an additive as claimed in any one of Claims 1 to 19.

**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**     -33-

Application number

GB 9223792.4

**Relevant Technical fields**

(i) UK Cl (Edition L ) C3J (JCE, JAX); C3K (KEC)

(ii) Int Cl (Edition 5 ) C08F

**Databases (see over)**

(i) UK Patent Office

(ii)

**Search Examiner**

K MACDONALD

**Date of Search**

25 MARCH 1993

Documents considered relevant following a search in respect of claims 1-34

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1475685 - (KODAK) EXS 1 & 2	AT LEAST CLAIM 1
X	GB 1428457 - (SANDOZ) Claim 1; page 3, lines 5-8	AT LEAST CLAIM 1
X	GB 0657081 - (DU PONT DENEMOURS) Claim 1; page 5, lines 64-65	AT LEAST CLAIM 1
X	EP 0003067 A1 - (METALLGESELLSCHAFT) Claims 1 & 8	AT LEAST CLAIM 1

Category	Identity of document and relevant passages - 34 -	Relevant to claim(s)

#### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

**Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.

**A:** Document indicating technological background and/or state of the art.

**P:** Document published on or after the declared priority date but before the filing date of the present application.

**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**&:** Member of the same patent family, corresponding document.

**Databases:** The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).